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SOUND ABSORPTION IN DILUTE
CHEMICALLY REACTING SYSTEMS

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ABSTRACT

A systematic theoretical development is presented for sound absorption in dilute chemically reacting systems when heat effects and other dissipative mechanisms, e.g. diffusion and viscous damping, are ignored.

A derivation is presented for the isothermal frequency dependent compressibility for such a system and the relation of this quantity to sound attenuation and the sound absorption spectrum.

The method is applied to several illustrative reaction mechanisms of interest. Particular attention is placed on the simplifications that arise when there is a single slow step in the reaction mechanism. The general case of coupled chemical reactions is treated and a prescription presented for determining the sound absorption coefficient.

The final section is concerned with sound absorption from chemical systems in steady states far from chemical equilibrium. For such systems the possibility exists that composition fluctuations will behave as chemical waves which will be exhibited by a distinctive splitting in the sound absorption spectrum.

I. Introduction

Sound absorption in chemically reactive fluids is a subject of interest to workers in a wide variety of fields, including chemistry, biology, and fluid mechanics. The subject also has some practical importance. In particular, sound absorption at relatively low frequency (below a few hundred kilohertz) in the ocean is markedly influenced by chemical relaxation between the prodigious number of different species (mostly ionic) that are present in sea water. Understandably, the subject has attracted the attention of the Navy and the Defense Advanced Research Projects Agency (DARPA) who have supported work in this area over the years. Substantial progress has been made in understanding the rather complicated chemistry and resulting sound absorption in sea water. However, some problems remain, notably the absorption at 1k-Hz attributable⁽¹⁾ to boric acid in sea water.

Consideration of this problem and the methods of analysis employed to interpret the sound propagation measurements indicates a need for a systematic development of the theory of sound absorption in chemically reacting systems. While theory is available in a number of sources⁽²⁻⁵⁾, the existing developments are either overly formal or difficult to penetrate. Moreover, the existing developments do not describe the approximations needed to reduce the general case of the influence of coupled reactions in solution on sound attenuation to the frequently encountered case where a single step in the reaction mechanism is slow and hence rate determining.

The purpose of this technical note is to provide a clear and direct theoretical development for sound absorption arising from chemical relaxation. Hopefully this development will be useful, not only for those working in sound attenuation in the oceans but also for others working on sound absorption in chemistry and biology.

The treatment presented is restricted to the circumstances most frequently encountered. It is assumed that dissipative transport processes other than chemical reaction, e.g. diffusion, thermal conduction, and viscous damping, can be ignored, which is usually the case at low frequencies. Thermal (enthalpic) effects due to heats of reaction are also ignored so the treatment is for isothermal conditions. Moreover, the analysis is restricted to dilute solutions so that all activity or concentration effects are ignored. All of these restrictive assumptions except for the last one (low concentration) can easily be relaxed.

In Section II, the pertinent solution thermodynamics is presented. Section III presents the pertinent relaxation equations for this problem, and in Section IV the determined frequency dependent isothermal compressibility is related to sound absorption. Section V is devoted to demonstrating for several mechanistic examples of interest how the method may be employed to determine the sound absorption spectrum. Section VI is concerned with a description of the general case that may be encountered in coupled chemical reactions where the assumption of a single slow step is not valid. The analysis of this section would be required if one wished to model a complex chemically reacting system, e.g. sea water, comprehensively and not

divide the problem so to speak, piecewise, where each frequency range is associated with a single dominant relaxation step. The final section is concerned with sound absorption from chemically reacting systems in a steady state, far from equilibrium, where the fluctuations in the chemical reaction behave as "chemical waves" and influence the attenuation of the sound waves accordingly. This last section contains material which should be of interest to the many workers who are currently devoting attention to non-linear chemically reacting systems.

II. Solution Thermodynamics

For a solution containing several components, the Gibbs free energy G is

$$\delta G = -S\delta T + V\delta p + \sum_i \mu_i \delta n_i + \mu_0 \delta n_0 \quad (2.1)$$

where S is the entropy, T the absolute temperature, V the volume, and p the pressure. Here μ_i is the chemical potential of solute species i and n_i the number of moles of species i ; μ_0 and n_0 denote respectively the chemical potential and moles of solvent, assumed inert.

We assume that the solute species are undergoing r chemical reactions of the form

$$\sum_i v_i^\alpha X_i = 0 \quad \alpha = 1, \dots, r \quad (2.2)$$

with the convention that the stoichiometric coefficients in the α^{th} reaction, v_i^α , are positive for products and negative for reactants.

We define the affinity of the α^{th} reaction A_α as

$$A_\alpha = \sum_i v_i^\alpha n_i \quad (2.3)$$

and the progress variable for the α^{th} reaction $\delta\lambda_\alpha$ as

$$\delta m_i^{(\alpha)} = \gamma_i^\alpha \delta \lambda_\alpha. \quad (2.4)$$

Since the interconversion of species can only occur by chemical reaction

$$\delta m_i = \sum_{\alpha} \delta m_i^{(\alpha)} \quad (2.5)$$

and Eq (2.1) may be expressed as

$$\delta G = -S\delta T + V\delta P + \sum_{\alpha} A_{\alpha} \delta \lambda_{\alpha} + \gamma_0 \delta n_0. \quad (2.6)$$

The solvent is assumed not to participate in any of the reactions.

At chemical equilibrium $(\delta G)_{T,P} = 0$ which yields the condition

$$A_{\alpha} = A_{\alpha}(T, P, \lambda^0) = 0 \quad (2.7)$$

which determines the equilibrium values of the variables $\lambda^0 = (\lambda_1^0, \dots, \lambda_r^0)$. These values will depend upon T and P , so $\lambda_{\alpha}^0 = \lambda_{\alpha}^0(T, P)$.

We shall assume that the species in solution that undergo chemical reaction exhibit ideal behavior so that

$$\mu_i(T, p, x_i) = \mu_i^0(T, p) + RT \ln x_i \quad (2.9)$$

where $x_i = n_i/n_0$ is the mole fraction of species i . It follows that we are restricting consideration to dilute solutions.

We shall be concerned with isothermal relaxation processes, i.e. temperature and enthalpy effects will be neglected. The formulation can easily be generalized to include these processes.

The differential change in the volume V is given by

(2.10)

$$\delta V = \left(\frac{\partial V}{\partial p} \right)_{T, \lambda} \delta p + \sum_{\alpha} \left(\frac{\partial V}{\partial \lambda_{\alpha}} \right)_{T, p, \lambda'} \delta \lambda_{\alpha}.$$

The equilibrium isothermal compressibility $\kappa_T(0)$ is defined by

$$\kappa_T(0) = - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T, \lambda=0} \quad (2.11)$$

and the "frozen" isothermal compressibility $\kappa_T(\infty)$ is defined by

$$\kappa_T(\infty) = - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T, \lambda} \quad (2.12)$$

so that we have the relation

$$X_T(0) = X_T(\infty) - \frac{1}{V} \sum_{\alpha} \left(\frac{\partial V}{\partial \lambda_{\alpha}} \right)_{T, p, \lambda} \left(\frac{\partial \lambda_{\alpha}}{\partial p} \right)_{T, A=0} \quad (2.13)$$

III Relaxation Behavior

We imagine a pressure wave of the form

$$\delta p(t) = \delta \hat{p}(\omega) \exp[i(\omega t - kx)] \quad (3.1)$$

imposed on the reacting mixture. This disturbance will instantaneously perturb the chemical environment. The species will interconvert in an effort to attain the new, momentarily established, local equilibrium condition $A_2(T, p+\delta p, \lambda + \delta \lambda) = 0$. For small disturbances the changed equilibrium is given by

$$\delta A_\alpha = \left(\frac{\partial A_\alpha}{\partial p} \right)_{T, \lambda} \delta p + \sum \left(\frac{\partial A_\alpha}{\partial \lambda_\beta} \right)_{T, p, \lambda} \delta \lambda_\beta. \quad (3.2)$$

The chemical species will not be able to follow the pressure disturbance instantaneously, and this will cause relaxation. The relaxation behavior is determined by the kinetic equations which are governed by the linear laws

(3.3)

$$\frac{1}{V} \frac{d \delta \lambda_\alpha}{dt} = - \sum_\beta L_{\alpha\beta} \delta A_\beta = - \sum_\beta L_{\alpha\beta} \left[\left(\frac{\partial A_\beta}{\partial P} \right)_{T, \lambda} \delta P + \sum_\gamma \left(\frac{\partial A_\beta}{\partial \lambda_\gamma} \right)_{T, P, \lambda} \delta \lambda_\gamma \right].$$

The factor V^{-1} included on the left hand side takes into account that the progress variables as defined here are extensive properties; the kinetic coefficients $L_{\alpha\beta}$ are intensive quantities. This expansion may be written in more compact vector notation

(3.4)

$$\frac{1}{V} \frac{d \delta \lambda}{dt} = - \underline{L} \cdot \underline{v} \delta P - \underline{L} \cdot \underline{U} \cdot \delta \lambda \frac{1}{V}$$

where

$$v_\alpha = \left(\frac{\partial A_\alpha}{\partial P} \right)_{T, \lambda} \quad (3.5)$$

and

$$U_{\alpha\beta} = V \left(\frac{\partial A_\alpha}{\partial \lambda_\beta} \right)_{T, P, \lambda} \quad (3.6)$$

In vector notation Eq. (2.10) is

$$\delta V = \left(\frac{\partial V}{\partial P} \right)_{T, \lambda} \delta P + \underline{V}^T \cdot \delta \underline{\lambda} \quad (3.7)$$

where use has been made of the Maxwell relation which follows from Eq. (2.6)

$$\left(\frac{\partial V}{\partial \lambda} \right)_{T, P, \underline{\lambda}} = \left(\frac{\partial A_\alpha}{\partial P} \right)_{T, \lambda} \equiv \underline{V}_\alpha. \quad (3.8)$$

At equilibrium $\delta \underline{\lambda} = 0$ and Eq. (3.4) yields the relation

$$- \underline{\lambda} = \underline{V} \cdot \left(\frac{\partial \underline{\lambda}}{\partial P} \right)_{T, A=0} \frac{1}{V} . \quad (3.9)$$

Thus, the compressibility relation, Eq. (2.13), can as well be expressed as

$$K_T(0) = K_T(\infty) + \underline{V}^T \cdot \underline{V}^{-1} \cdot \underline{\lambda}, \quad (3.10)$$

a relation that will prove useful shortly.

The imposed pressure will induce a steady state response in the volume and progress variables given by

$$\delta V = \hat{\delta V} \exp[i(wt - kx)] \text{ and } \delta \underline{\lambda} = \hat{\delta \underline{\lambda}} \exp[i(wt - kx)] \quad (3.11)$$

respectively. The steady state response for isothermal changes in volume is

$$\delta \hat{V} = \left(\frac{\partial V}{\partial p} \right)_{T, \underline{\lambda}} \delta \hat{p} + \underline{v}^T \cdot \delta \hat{\underline{\lambda}}. \quad (3.12)$$

We may solve for $\delta \hat{\underline{\lambda}}$ by substitution Eq. (3.11) in Eq. (3.12); the result is

$$\delta \hat{\underline{\lambda}} = -V \left[i\omega \underline{I} + \underline{L} \cdot \underline{\Omega} \right]^{-1} \cdot \underline{L} \cdot \underline{v} \delta \hat{p}. \quad (3.13)$$

Before proceeding, it is useful to write Eq. (3.13) in terms of more familiar rate expressions by defining the kinetic matrix

$$\underline{M} = \underline{L} \cdot \underline{\Omega} \quad (3.14)$$

then Eq. (3.13) takes the form

$$\delta \hat{\underline{\lambda}} = -V \left[i\omega \underline{I} + \underline{M} \right]^{-1} \cdot \underline{M} \cdot \underline{\Omega}^{-1} \cdot \underline{v} \delta \hat{p}. \quad (3.15)$$

In terms of time Eq. (3.15) corresponds to

$$\frac{d\delta\lambda}{dt} = -M \cdot \delta\lambda - V M \cdot \delta\zeta \quad (3.16)$$

where $\delta\zeta$ are "imposed" concentration differences induced by the pressure wave perturbation

$$\delta\zeta = \underline{M}^{-1} \cdot \underline{V} \delta\hat{p}. \quad (3.17)$$

We continue by eliminating $\delta\lambda$ between Eqs. (3.13) and (3.12) thus obtaining a relation between $\delta\hat{V}$ and $\delta\hat{p}$:

$$\delta\hat{V} = \delta\hat{p} \left\{ \left(\frac{\partial V}{\partial p} \right)_{T, \lambda} - V \underline{V}^T \cdot [i\omega \underline{I} + \underline{M}]^{-1} \cdot \underline{M} \cdot \underline{M}^{-1} \cdot \underline{V} \right\}. \quad (3.18)$$

The quantity $\delta\hat{V}/\delta\hat{p}$ can be related to the frequency dependent isothermal compressibility

$$\chi_T(\omega) = -\frac{1}{V} \left(\frac{\delta\hat{V}}{\delta\hat{p}} \right)_T. \quad (3.19)$$

Then Eq. (3.18) may be written as

(3.20)

$$K_T(\omega) = K_T(\infty) + \underline{X}^T \cdot [i\omega \underline{I} + \underline{M}]^{-1} \cdot \underline{M} \cdot \underline{\Omega}^{-1} \cdot \underline{X}.$$

Alternatively, Eq. (3.10) may be employed to express $K_T(\omega)$ as

(3.21)

$$K_T(\omega) = K_T(0) - i\omega \underline{X}^T \cdot [i\omega \underline{I} + \underline{M}]^{-1} \cdot \underline{\Omega}^{-1} \cdot \underline{X}.$$

In the limit $\omega \rightarrow 0$, $K_T(\omega) \rightarrow K_T(0)$, and in the limit $\omega \rightarrow \infty$, $K_T(\omega) \rightarrow K_T(\infty)$.

This expression for $K_T(\omega)$ is the central starting point for the investigation of sound absorption in chemically reacting fluids. It is important to bear in mind the restrictive assumptions under which this result has been obtained. In particular, temperature effects have been ignored and local equilibrium conditions have been assumed. In Section VI we will indicate how this expression can most easily be evaluated for complex chemically reacting systems of interest.

IV Relation to Sound Attenuation

The isothermal sound speed C_T is given by

$$C_T^2 = (\rho_0 \chi_T)^{-1} \quad (4.1)$$

and the pressure satisfies the wave equation

$$\frac{\partial^2 \delta p}{\partial t^2} = C_T^2 \frac{\partial^2 \delta p}{\partial x^2} \quad (4.2)$$

when viscous, diffusive, and heat dissipation effects are ignored.

For a pressure wave of the form Eq. (3.1) one obtains the dispersion relation

$$\omega^2 = C_T^2 k^2 \quad (4.3)$$

For the case of chemical relaxation the corresponding dispersion relation is

$$\omega^2 = \frac{1}{\rho_0 \chi_T(\omega)} k^2 = C_T^2(\omega) k^2 \quad (4.4)$$

and the frequency dependent compressibility leads to both sound absorption and velocity dispersion. For the case of an impressed pressure wave disturbance of real frequency ω , the complex frequency

dependency in $\kappa_T(\omega)$ will force κ to become complex.

Let

$$\kappa = \kappa' - i \kappa'' \quad (4.5)$$

and seek a solution to Eq. (4.4) for the imaginary part, κ'' . If we express $\kappa_T(\omega)$ in real and imaginary parts

$$\kappa_T(\omega) = \kappa'_T(\omega) - i \kappa''_T(\omega) \quad (4.6)$$

one finds

$$\rho_0 \omega^2 [\kappa'_T(\omega) - i \kappa''_T(\omega)] = (\kappa')^2 \left[1 - 2i \frac{\kappa''}{\kappa'} - \left(\frac{\kappa''}{\kappa'} \right)^2 \right]. \quad (4.7)$$

Generally, one is justified in assuming that the characteristic length for attenuation $(\kappa'')^{-1}$ is large compared to the wave length $(\kappa')^{-1}$ so that terms of order $(\kappa''/\kappa')^2$ in Eq. (4.7) may be ignored. Under these circumstances one finds

$$(\kappa')^2 = \rho_0 \omega^2 \kappa'_T(\omega) \quad (4.8)$$

and

$$k'' = \frac{1}{2k'} \rho_0 \omega^2 \chi_T''(\omega) \quad (4.9)$$

The speed of sound is simply related to k' according to

$$C_T^2(\omega) = \frac{\omega^2}{(k')^2} = [\rho_0 \chi_T'(\omega)]^{-1} \quad (4.10)$$

The resulting expression for the pressure wave

$$\delta p(x,t) = \hat{\delta p}(\omega) \exp[i(\omega t - k' x)] \exp[-k'' x] \quad (4.11)$$

clearly identifies k'' as the attenuation in the medium. The adsorption per wave length $\alpha(\omega)$ is defined

$$\alpha(\omega) = k'' \lambda = 2\pi k''/k' = \frac{\pi \chi_T''(\omega)}{\chi_T'(\omega)} \quad (4.12)$$

Consider the simple case of single relaxation time where

$$\chi_T(\omega) = \chi_T(\infty) + A \frac{1}{1+i\omega\tau} \quad (4.13)$$

then

$$\chi'_T(\omega) = \chi'_T(\infty) + \frac{A}{1 + (\omega\tau)^2} \quad (4.14)$$

and

$$\chi''_T(\omega) = \frac{A\omega\tau}{1 + (\omega\tau)^2} \quad (4.15)$$

so that

$$C_T(\omega) \approx \frac{1}{\sqrt{3\chi'_T(\infty)}} \left[1 - \frac{(A/2)\chi'_T(\infty)}{1 + (\omega\tau)^2} \right] \quad (4.16)$$

and

$$\alpha \approx \frac{\pi A}{\chi'_T(\infty)} \frac{\omega\tau}{1 + (\omega\tau)^2} \quad (4.17)$$

In the general case of many relaxation times

$$\chi_T(\omega) = \chi_T(\infty) + \sum_e A_e \frac{1}{1 + i\omega\tau_e} \quad (4.18)$$

the calculation of $\alpha(\omega)$ and $C_T(\omega)$ presents an algebraic task that, in general, will require numerical calculation. However, for many cases of interest the dispersion in velocity [$A_\ell/\kappa_T(\infty)$] will be quite small and $\alpha(\omega)$ can be approximated by

$$\alpha(\omega) \approx \frac{\pi}{\kappa_T(\infty)} \sum_{\ell} A_{\ell} \frac{\omega \tau_{\ell}}{1 + (\omega \tau_{\ell})^2} \quad (4.19)$$

V Some Examples

First consider the case where there is no coupling between the reactions. Then

$$L = L_{\alpha\alpha} \delta_{\alpha\beta}, \quad L' = L_{\alpha\alpha} \delta_{\alpha\beta}, \text{ and } L^{-1} = L_{\alpha\alpha}^{-1} \delta_{\alpha\beta} \quad (5.1)$$

and it follows from Eq. (3.20) that

$$X_T(\omega) = X_T(\infty) + \sum_{\alpha} \left[\left(\frac{\partial V}{\partial \lambda_{\alpha}} \right)_{T, p, \lambda}^2 / V \left(\frac{\partial A_{\alpha}}{\partial \lambda_{\alpha}} \right)_{T, p, \lambda} \right] \frac{1}{1 + i\omega \zeta_{\alpha}}. \quad (5.2)$$

Note that this expression has the form of Eq. (4.18).

For a single reaction, the result of Eq. (3.20) or (5.2) is

$$X_T(\omega) = X_T(\infty) + \left[\left(\frac{\partial V}{\partial \lambda} \right)_{T, p}^2 / V \left(\frac{\partial A}{\partial \lambda} \right)_{T, p} \right] \frac{1}{1 + i\omega \zeta}. \quad (5.3)$$

V.A. First Order Equilibria

Consider a simple unimolecular equilibrium



For this mechanism

$$A = \nu_B^0 - \nu_A^0 + RT \ln x_B - RT \ln x_A \quad (5.5)$$

or since the total number of moles is constant

$$A = \nu_B^0 - \nu_A^0 + RT \ln M_B - RT \ln M_A \quad (5.6)$$

where M_A and M_B are the number of moles in the volume V . The progress variable is simply

$$\delta \lambda = \delta M_B = -\delta M_A \quad (5.7)$$

The derivatives required for the evaluation of Eq. (5.3) are easily found.

$$\left(\frac{\partial V}{\partial \lambda} \right)_{T, P} = \left(\frac{\partial A}{\partial P} \right)_{T, \lambda} = (\nu_B^0 - \nu_A^0) \equiv \Delta \nu \quad (5.8)$$

and

$$\left(\frac{\partial A}{\partial \lambda} \right)_{T, P} = RT \left[\frac{1}{M_B^0} + \frac{1}{M_A^0} \right] = \frac{RT}{M} \left[\frac{1}{x_B^0} + \frac{1}{x_A^0} \right] \quad (5.9)$$

with $M = m_A^0 + m_B^0 + m_0$, the total number of moles in volume V in the solution.

It should be noted that

$$\Delta v = \left(\frac{\partial \Delta P^0}{\partial P} \right)_T$$

and since the equilibrium constant K is

$$K = \exp \left[- \Delta P^0 / RT \right]$$

we may find Δv from K according to

$$\Delta v = - RT \left(\frac{\partial \ln K}{\partial P} \right)_T$$

The relaxation time must be determined from the kinetic equations which we write in terms of the moles of species in the volume V instead of the concentrations. This is required because the progress variables have been defined as extensive quantities.

$$\frac{dM_A}{dt} = - k_1 M_A + k_{-1} M_B \quad (5.10)$$

$$\frac{dM_B}{dt} = + k_1 M_A - k_{-1} M_B$$

Note that at equilibrium

(5.11)

$$k_1 M_A^0 = k_{-1} M_B^0 \quad \text{or} \quad \frac{M_B^0}{M_A^0} = \frac{x_B^0}{x_A^0} = \frac{k_1}{k_{-1}} = K_1$$

so that in terms of deviations from equilibrium Eq. (5.10) is

(5.12)

$$\frac{d \delta M_A}{dt} = -k_1 \delta M_A + k_{-1} \delta M_B$$

$$\frac{d \delta M_B}{dt} = +k_1 \delta M_A - k_{-1} \delta M_B,$$

In terms of the progress variable, Eq. (5.7) one obtains a single equation

(5.13)

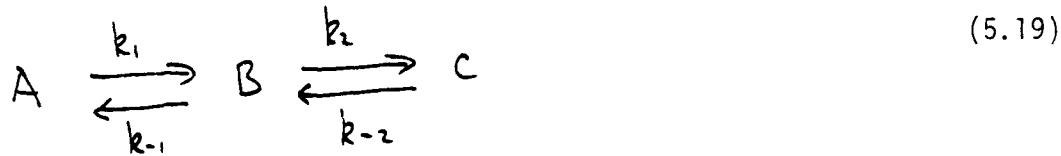
$$\frac{d \delta \lambda}{dt} = - (k_1 + k_{-1}) \delta \lambda$$

which immediately identifies the relaxation time as $\tau^{-1} = (k_1 + k_{-1})$.

In sum, $\chi_T(\omega)$ is

$$\chi_T(\omega) = \chi_T(\infty) + \frac{(\Delta V)^2}{R T V} \left[\frac{x_A^0 x_B^0}{(x_A^0 + x_B^0)} \right] \frac{1}{1 + i\omega [k_1 + k_{-1}]^{-1}} \quad (5.14)$$

where $V = V/M$.

V.B. Coupled First Order Equilibrium With a Slow StepWe next consider the coupled reaction scheme

which has the following kinetic equations (in terms of moles in the volume V)

$$\frac{dM_A}{dt} = -k_1 M_A + k_{-1} M_B \tag{5.17}$$

$$\frac{dM_B}{dt} = +k_1 M_A - (k_{-1} + k_2) M_B + k_{-2} M_C$$

$$\frac{dM_C}{dt} = +k_2 M_B - k_{-2} M_C$$

and two progress variables

$$-\delta\lambda_1 = \delta M_A \quad \delta\lambda_2 = \delta M_C \quad \text{with } \delta M_B = \delta\lambda_1 - \delta\lambda_2 \tag{5.18}$$

$$-\delta\lambda_1 = \delta M_A \quad \delta\lambda_2 = \delta M_C \quad \text{with } \delta M_B = \delta\lambda_1 - \delta\lambda_2 ,$$

In terms of the progress variables one has

$$\frac{d\delta\lambda_1}{dt} = - (k_1 + k_{-1}) \delta\lambda_1 + k_{-1} \delta\lambda_2 \tag{5.19}$$

$$\frac{d\delta\lambda_2}{dt} = k_2 \delta\lambda_1 - (k_2 + k_{-2}) \delta\lambda_2 ,$$

We consider the special case where the second reaction is slow compared to the first. In this case one may set $(d\delta\lambda/dt) = 0$ in Eq. (5.19) and obtain the relation

$$\delta\lambda_1 = \frac{k_{-1}}{k_1 + k_{-1}} \delta\lambda_2 \quad (5.20)$$

and hence

$$\frac{d\delta\lambda_2}{dt} = -k_{-2} \left[1 + K_2 - \frac{K_2}{1 + K_1} \right] \delta\lambda_2 \quad (5.21)$$

where we have introduced the equilibrium constants

$$K_1 = \frac{k_1}{k_{-1}} = \frac{M_B^\circ}{M_A^\circ} \quad K_2 = \frac{k_2}{k_{-2}} = \frac{M_C^\circ}{M_B^\circ} \quad (5.22)$$

Thus the slow relaxation is characterized by the relaxation time

$$\tau^{-1} = k_{-2} \left[1 + \frac{K_2 K_1}{1 + K_1} \right] \quad (5.23)$$

The effect of assuming the rapid equilibration of the first step [and the steady state approximation (dS_1/dt)] is that the coupled mechanism may be effectively reduced to a single step reaction mechanism



where

$$k_2^* = \frac{k_2 K_1}{1 + K_1} \quad (5.25)$$

with kinetics

$$\frac{dM_{A^*}}{dt} = -k_2^* M_{A^*} + k_{-2} M_C \quad (5.26)$$

$$\frac{dM_C}{dt} = +k_2^* M_{A^*} - k_{-2} M_C$$

or, in terms of progress variables

$$\frac{dS\lambda}{dt} = -(k_2^* + k_{-2}) S\lambda \quad (5.27)$$

which is identical to Eq. (5.21).

We note that for the effective single step process, Eq. (5.24) the equilibrium constant is

$$\frac{n_c^0}{M_{A^*}^0} = \frac{k_2^*}{k_{-2}} = K_2^* = \frac{K_2 K_1}{1 + K_1} \quad (5.28)$$

We can determine the effective volume change for the reaction in the normal way

$$\Delta V^* = \frac{1}{RT} \left(\frac{\partial \ln K_2^*}{\partial P} \right)_T \quad (5.29)$$

which immediately yields

$$\Delta V^* = \Delta V_2 + \Delta V_1 - \frac{K_1}{1 + K_1} \Delta V_1 = \Delta V_2 + \frac{\Delta V_1}{1 + K_1} \quad (5.30)$$

where

$$\Delta V_1 = V_B^0 - V_A^0 \quad \text{and} \quad \Delta V_2 = V_c^0 - V_A^0 .$$

We may now express the frequency dependent isothermal compressibility for this effective one-step process as

$$\kappa_T(\omega) = \kappa_T(\infty) + \frac{(\Delta V^*)^2}{RTV} \left[\frac{x_{A^*}^0 x_c^0}{x_{A^*}^0 + x_c^0} \right] \frac{1}{1 + i\omega\gamma}$$

in analogy to Eq. (5.14), where τ is given by Eq. (5.23) and Δv^* by Eq. (5.32). It follows from Eq. (4.12) that in the limit of low dispersion the absorption coefficient is

$$\alpha(\omega) = \frac{\pi (\Delta v^*)^2}{K_T(0) RT \nu} \left[\frac{X_A^* X_c^0}{X_A^0 + X_c^0} \right] \frac{\omega^2}{1 + (\omega \tau)^2} \quad (5.31)$$

which may be written in the alternative form

$$\alpha(\omega) = \frac{\pi (\Delta v^*)^2}{RT} \rho_c C_T^2(0) \left[\frac{C_A^0 C_c^0}{C_A^0 + C_c^0} \right] \frac{1}{\tau} \frac{\omega^2}{1 + (\omega \tau)^2} \quad (5.32)$$

where C_A^0 , C_c^0 etc. are the equilibrium concentration. Using the definition of τ Eq. (5.23) and, according to Eq. (5.28)

$$K_2^* = \frac{C_c^0}{C_A^*}$$

this expression may be simplified to

$$\alpha(\omega) = \frac{\pi (\Delta v^*)^2}{RT} \rho_c C_T^2(0) k_{-2} C_c^0 \frac{\omega \tau^2}{1 + (\omega \tau)^2} \quad (5.33)$$

For purposes of later comparison to the work of others we note that

(5.34)

$$C_c^0 = \frac{k_2}{1+k_2} [C_B^0 + C_C^0]$$

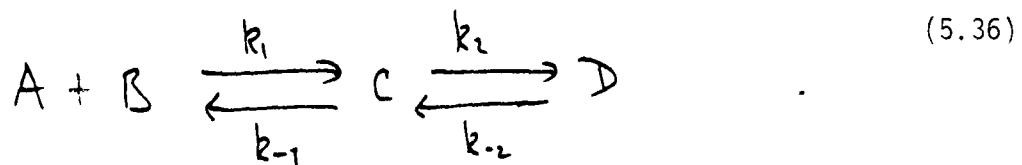
so that

(5.35)

$$\alpha(\omega) = \frac{\pi (\Delta \nu^*)^2 \rho_0 C_T^2 (D)}{R T} \frac{k_{-2} k_2}{1+k_2} (C_B^0 + C_C^0) \frac{\omega \tau^2}{1 + (\omega \tau)^2}$$

V.C. More Complicated Coupled Equilibria with a Slow Step

We note that more complicated reaction schemes that contain a slow step may be treated by the same procedure as described in the previous section. As a final example we consider the scheme extensively discussed by Eigen and de Maeyer⁽⁵⁾ and employed by Mellen et al. in their investigations of the low frequency sound absorption in sea water⁽¹⁾. The scheme is



The kinetic equations are

(5.37)

$$\frac{dA}{dt} = -k_1 AB + k_{-1} C = \frac{dB}{dt}$$

$$\frac{dc}{dt} = k_1 AB - (k_{-1} + k_2)c + k_{-2}D$$

$$\frac{dD}{dt} = + k_2 c - k_{-2} D$$

where we have simplified notation by writing $A = C_A$ etc. In terms of small deviations from equilibrium, we have

$$\frac{d\delta A}{dt} = - k_1 (A_0 \delta B + B_0 \delta A) + k_{-1} \delta C = \frac{d\delta B}{dt} \quad (5.38)$$

$$\frac{d\delta C}{dt} = + k_1 (A_0 \delta B + B_0 \delta A) - (k_{-1} + k_2) \delta C + k_{-2} \delta D$$

$$\frac{d\delta D}{dt} = + k_2 \delta C - k_{-2} \delta D$$

For this reaction the progress variables are

(5.39)

$$\delta A = \delta B = - \frac{\delta \lambda_1}{V} \quad \delta D = \frac{\delta \lambda_2}{V} \quad \delta C = V^{-1} (\delta \lambda_1, -\delta \lambda_2)$$

where the factor V is included in order to relate the change in concentrations in the volume V to the change in the extensive progress variables. So we obtain

$$\frac{d\delta \lambda_1}{dt} = - [k_1 (A_0 + B_0) + k_{-1}] \delta \lambda_1 + k_{-1} \delta \lambda_2 \quad (5.40)$$

$$\frac{d\delta \lambda_2}{dt} = + k_2 \delta \lambda_1 - (k_2 + k_{-2}) \delta \lambda_2$$

which is precisely in the same form as Eq. (5.19), if we make the identification

(5.41)

$$\hat{k}_1 = k_1 (A_0 + B_0)$$

If again we assume the second step is rate limiting and set $(dS\lambda_1/dt) = 0$, we find, exactly as in the previous example, that

(5.42)

$$\tau^{-1} = k_{-2} \left[1 + \frac{\hat{K}_1 K_2}{1 + \hat{K}_1} \right]$$

where

$$\hat{K}_1 = \frac{\hat{k}_1}{k_{-1}} = k_1 (A_0 + B_0) \quad (5.43)$$

We may again view the rapid first step as establishing an equilibrium that leads to an effective single step mechanism of the form



with, now, [c.f. Eq. (5.25)]

$$k_2^* = k_2 \hat{K}_1 / (1 + \hat{K}_1) \quad (5.45)$$

and associated equilibrium constant [c.f. Eq. (5.28)]

$$K_2^* = \frac{k_2^*}{k_{-2}} = K_2 \hat{K}_1 / (1 + \hat{K}_1). \quad (5.46)$$

It follows that for this effective one-step reaction the change in volume is

$$\Delta V^* = \Delta V_2 + \Delta V_1 / (1 + \hat{K}_1). \quad (5.47)$$

The remainder of the analysis for the absorption spectrum follows the preceding example exactly. We obtain the result

$$\alpha(\omega) = \frac{\pi (\Delta V^*)^2 \rho_0 C_T^2 / \tau}{RT} \frac{k_{-2} k_2}{1 + K_2} \frac{(C_e^0 + C_g^0)}{1 + \omega \tau}$$

with τ given by Eq. (5.42). This result is identical to that obtained by Mellen et al.⁽¹⁾

It has been correctly pointed out that this method may be applied to other coupled reaction mechanism (provided, presumably, that unstable states are not present) where a single slow step is rate limiting. This result is presented next.

Consider the general case where the slow step is first order between species Y and Z. Each of these species may be involved either directly or indirectly, through coupling to other species, in reactions that are rapid compared to the interconversion.



If one writes the entire reaction mechanisms in terms of the pertinent rate equations for the progress variable λ and sets all $(d\lambda/dt) = 0$ except for the variable λ characterizing the slow step Eq. (5.48), one arrives at the effective rate equation



which corresponds to the reaction scheme:

$$\frac{d\delta\lambda}{dt} = - (k_1^* + k_{-1}^*) \delta\lambda. \quad (5.50)$$

The rates k_1^* and k_{-1}^* will be found as a function of the rate coefficients, equilibrium constants, and equilibrium concentrations of other species in the mechanism. The change in volume ΔV^* is given by

$$\Delta V^* = \frac{1}{RT} \left(\frac{\partial \ln K^*}{\partial p} \right)_T \quad (5.51)$$

where

$$K^* = [k_1^* / k_{-1}^*] \quad (5.52)$$

and the absorption spectrum is simply expressed as

$$K_T(\omega) = K_T(\infty) + \frac{(\Delta v^*)^2}{RTv} \left[\frac{X_{Y^*}^0 X_{Z^*}^0}{X_{Y^*}^0 + X_{Z^*}^0} \right] \frac{1}{1 + i\omega [k_1^* + k_{-1}^*]^{-1}}. \quad (5.53)$$

Thus we have presented an explicit method for determining the absorption coefficient for the case of a single slow first order step in a complex coupled chemical reacting system. The method is easily generalized to the case where the slow step involves the species Y and Z in higher order reactions.

VI Analysis of the General Case of Coupled Reactions

We return to Eq. (3.20), the general expression for $\kappa_T(\omega)$ for a coupled chemical system. We shall obtain an expression for $\kappa_T(\omega)$ and hence $\alpha(\omega)$ in terms of the eigenvectors $\underline{\psi}$ and eigenvalues λ of the kinetic matrix \underline{M} . In general \underline{M} is not a symmetric matrix (reflecting the fact that equilibrium constants are not unity) so it is necessary to be concerned with both right and left handed eigenvalues of \underline{M} :

$$\underline{M} \cdot \underline{\psi}_n^R = \lambda_n \underline{\psi}_n^R \quad (6.1)$$

and

$$(\underline{\psi}_n^L)^T \cdot \underline{M} = \lambda_n (\underline{\psi}_n^L)^T ; \quad (6.2)$$

alternatively

$$\underline{M}^T \cdot \underline{\psi}_n^L = \lambda_n \underline{\psi}_n^L , \quad (6.3)$$

These eigenvectors are constructed to be orthonormal

$$(\underline{\psi}_m^R)^T \cdot \underline{\psi}_n^L = \delta_{mn} \quad (6.4)$$

and form a complete set in the vector space of the r chemical reactions.

Thus we may expand any vector \underline{t} as

$$\underline{t} = \sum_m a_m \underline{\psi}_m^R \quad (6.5)$$

and the coefficient a_m will be given by

$$a_m = (\underline{\psi}_m^L)^T \cdot \underline{t} \quad (6.6)$$

Alternatively the vector \underline{S}^T may be expanded as

$$\underline{S}^T = \sum_m b_m (\underline{\psi}_m^L)^T \quad (6.7)$$

and the coefficient b_m will be given by

$$b_m = (\underline{S}^T \cdot \underline{\psi}_m^R) \quad (6.8)$$

We shall expand the vectors $(\underline{S}^{-1} \cdot \underline{v})$ according to Eq. (6.5) and the vector \underline{v} according to Eq. (6.7) and substitute these expressions into Eq. (3.20). If we make use of Eqs. (6.1) and (6.4) we obtain

$$X_T(\omega) = X_T(\infty) + \sum_n b_n \frac{\lambda_n}{i\omega + \lambda_n} a_n \quad (6.9)$$

where

$$b_n = (\underline{v}^T \cdot \underline{\psi}_n^R) \quad \text{and} \quad a_n = (\underline{\psi}_n^L)^T \cdot \underline{U}^{-1} \cdot \underline{v}. \quad (6.10)$$

It is immediately apparent that the (real) eigenvalues of the linearized kinetic matrix \underline{M} are the relaxation times of the coupled chemically reacting system

$$\tau_n^{-1} = \lambda_n \quad (6.11)$$

so that

$$X_T(\omega) = X_T(\infty) + \sum_n b_n \frac{1}{1 + i\omega\tau_n} a_n \quad (6.12)$$

We next demonstrate that $b_n = a_n$. Since $\underline{M} = \underline{U} \cdot \underline{J} \cdot \underline{U}^{-1}$, one has from Eq. (6.1) after multiplying both sides of the equation by $\underline{U}^{1/2}$:

$$[\underline{U}^{1/2} \cdot \underline{U} \cdot \underline{U}^{1/2}] \cdot [\underline{U}^{1/2} \cdot \underline{\psi}_n^R] = \lambda_n (\underline{U}^{1/2} \cdot \underline{\psi}_n^R). \quad (6.13)$$

Thermodynamic stability requires that $\underline{\underline{L}}$ is symmetric, i.e. $\underline{\underline{L}}^T = \underline{\underline{L}}$ and it is an easy matter to show from Eqs. (2.6) and (3.6) that $\underline{\underline{R}}$ is symmetric. Accordingly, it follows that $\underline{\underline{M}}^T = \underline{\underline{R}} \cdot \underline{\underline{L}} \cdot \underline{\underline{R}}^T = \underline{\underline{R}} \cdot \underline{\underline{L}} \cdot \underline{\underline{R}}$. One has from Eq. (6.3) after multiplying both sides of the equation by $\underline{\underline{R}}^{-1/2}$:

$$[\underline{\underline{R}}^{1/2} \cdot \underline{\underline{L}} \cdot \underline{\underline{R}}^{1/2}] \cdot [\underline{\underline{R}}^{-1/2} \cdot \underline{\underline{\psi}}_n^L] = \lambda_n (\underline{\underline{R}}_n^{-1/2} \cdot \underline{\underline{\psi}}_n^L). \quad (6.14)$$

It follows from Eqs. (6.13) and (6.14) (the matrix $\underline{\underline{M}}$ has no zero eigenvalues) that

$$\underline{\underline{R}}^{-1/2} \cdot \underline{\underline{\psi}}_n^L = \underline{\underline{R}}^{1/2} \cdot \underline{\underline{\psi}}_n^R. \quad (6.15)$$

We may write

$$\underline{\underline{\psi}}_n^R = \underline{\underline{R}}^{-1} \cdot \underline{\underline{\psi}}_n^L \quad \text{and} \quad (\underline{\underline{\psi}}_n^R)^T = (\underline{\underline{\psi}}_n^L)^T \cdot \underline{\underline{R}}^{-1} \quad (6.16)$$

where in the second relation we have used the fact that $[\underline{\underline{R}}^{-1}]^T = \underline{\underline{R}}^{-1}$.

Since

$$b_n = (\underline{\underline{\psi}}^T \cdot \underline{\underline{\psi}}_n^R) = (\underline{\underline{\psi}}_n^R)^T \cdot \underline{\underline{\psi}} \quad (6.17)$$

we may substitute Eq. (6.16) to demonstrate that

$$b_n = (\underline{U}^T \cdot \underline{\psi}_n^R) = (\underline{\psi}_n^L)^T \cdot \underline{U}^{-1} \cdot \underline{U} = a_n .$$

Thus Eq. (6.12) becomes

$$X_T(\omega) - X_T(\infty) = \sum_n b_n^2 \frac{1}{1 + i\omega\gamma_n} , \quad (6.18)$$

In sum, in order to calculate $X_T(\omega)$ for coupled chemical reactions one must know \underline{U} and the eigenvalues and eigenvectors of \underline{M} . While this will not always prove possible to do analytically, it can easily be accomplished on a computer.

As an example we compute the exact $X_T(\omega)$ for the mechanism considered by Mellen et al. displayed in Eq. (5.36). The matrix \underline{M} is simply

$$\underline{M} = \begin{bmatrix} (\hat{k}_1 + k_{-1}) & -k_{-1} \\ -k_2 & (k_2 + k_{-2}) \end{bmatrix} , \quad (6.19)$$

The eigenvalues are found from the equation $\det [\lambda \mathbb{I} - \underline{M}] = \det [\lambda \mathbb{I} - \underline{M}^T] = 0$:
(6.20)

$$\det [\lambda \mathbb{I} - \underline{M}] = \det \begin{bmatrix} \lambda - (\hat{k}_1 + k_{-1}) & k_{-1} \\ k_2 & \lambda - (k_2 + k_{-2}) \end{bmatrix}.$$

The two roots will occur in the vicinity of $\lambda \sim (\hat{k}_1 + k_{-1})$ and $\lambda \sim (k_2 + k_{-2})$. If we are interested in the second root and $(\hat{k}_1 + k_{-1}) \gg (k_2 + k_{-2})$, i.e. the first reaction step is fast compared with the second, one is justified in dropping the λ in the upper left hand corner of Eq. (5.42). This yields a single eigenvalue which, as expected, is identical to Eq. (5.42), for the case of a single, slow rate determining step considered in Sec. V.C.

The eigenvalues are

$$\lambda_{\pm} = \frac{m_1 + m_2}{2} \pm \frac{1}{2} \sqrt{(m_1 - m_2)^2 + 4k_2 k_{-1}} \quad (6.21)$$

where

$$m_1 = \hat{k}_1 + k_{-1} \quad \text{and} \quad m_2 = k_2 + k_{-2} \quad (6.22)$$

The eigenvalues are plainly real and positive.

Note that for $M_1 \gg M_2$, λ approaches the relaxation time Eq. (5.42).

The eigenvalues of the matrix

$$\underline{M} = \begin{bmatrix} m_1 & -k_{-1} \\ -k_2 & m_2 \end{bmatrix} \quad (6.23)$$

may be expressed in terms of the parameters

$$\omega = m_1 + m_2 \quad (6.24)$$

$$\Delta = m_2 - m_1$$

$$r = [\Delta^2 + 4k_1 k_{-1}]$$

so that

$$\lambda_{\pm} = \frac{\omega}{2} \pm \frac{1}{2} \sqrt{r} \quad (6.25)$$

and

$$\det(\underline{M}) = \lambda_+ \lambda_- = \frac{\omega^2}{4} - \frac{r}{4} = m_1 m_2 - k_{-1} k_2. \quad (6.26)$$

The right hand eigenvectors are

$$\underline{\psi}_+^R \propto \begin{pmatrix} k_+ \\ \frac{\Delta - \sqrt{r}}{2} \end{pmatrix} \quad (6.27a)$$

corresponding to λ_+ and

$$\underline{\psi}_-^R \propto \begin{pmatrix} k_- \\ \frac{\Delta + \sqrt{r}}{2} \end{pmatrix} \quad (6.27b)$$

corresponding to λ_- .

The left hand eigenvectors are

$$\underline{\psi}_+^L \propto \begin{pmatrix} k_+ \\ \frac{\Delta - \sqrt{r}}{2} \end{pmatrix} \quad (6.28a)$$

corresponding to λ_+ and

$$\underline{\psi}_-^L \propto \begin{pmatrix} k_- \\ \frac{\Delta + \sqrt{r}}{2} \end{pmatrix} \quad (6.28b)$$

corresponding to λ_- .

Note that

$$(\underline{\psi}_+^L)^T \cdot \underline{\psi}_-^R = (\underline{\psi}_-^L)^T \cdot \underline{\psi}_+^R = 0 \quad (6.29)$$

Normalization of these eigenvectors is accomplished by requiring

$$(\underline{\psi}_+^L)^T \cdot \underline{\psi}_+^R = (\underline{\psi}_-^L)^T \cdot \underline{\psi}_-^R = 1$$

so that

$$c_+^2 = k_1 k_2 + \frac{1}{4} (\Delta - \Gamma)^2 \quad (6.30a)$$

and

$$c_-^2 = k_1 k_2 + \frac{1}{4} (\Delta + \Gamma)^2. \quad (6.30b)$$

According to Eq. (6.10)

$$b_+ = (\underline{v}^T \cdot \underline{\psi}_+^R) = \frac{1}{c_+} \left[k_1 \Delta v_I + \left(\frac{\Delta - \Gamma}{2} \right) \Delta v_{II} \right] \quad (6.31a)$$

and

$$b_- = (\underline{v}^T \cdot \underline{\psi}_-^R) = \frac{1}{c_-} \left[k_1 \Delta v_I + \left(\frac{\Delta + \Gamma}{2} \right) \Delta v_{II} \right]. \quad (6.31b)$$

Thus we have found the complete solution to the reaction mechanism Eq. (5.36). The frequency dependent compressibility is [from Eq. (6.18)] simply

$$K_T(\omega) = K_T(\infty) + b_+^2 \frac{1}{1+i\omega\tau_+} + b_-^2 \frac{1}{1+i\omega\tau_-}$$

where b_{\pm} is given by Eq. (6.31) and $\tau_{\pm}^{-1} = \lambda_{\pm}$ is given by Eq. (6.21).

It is evident that much more complicated reaction schemes, such as those which characterize chemical relaxation in the ocean, can easily be treated by the method exactly, if use is made of a computer to determine the eigenvectors and eigenvalues for a particular reaction mechanism with known rate coefficients. Accordingly, it would be possible and desirable to attempt to fit the entire spectrum of sea water absorption exactly in order to verify the accuracy of existing assumed chemical reaction models.

VII Sound Absorption from Systems Far From Equilibrium

For systems near chemical equilibrium, thermodynamics assures that the relaxation times (eigenvalues) encountered are real and positive. However, in a steady state, far from equilibrium a coupled non-linear reaction scheme may exhibit more complex behavior.

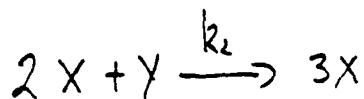
Fluctuations from the steady state may be stable $[Re(\lambda_m) > 0]$, unstable $[Re(\lambda_m) < 0]$, or marginally stable $[Re(\lambda_m) = 0]$. In addition fluctuations may exhibit oscillatory behavior $[Im(\lambda_m) \neq 0]$.

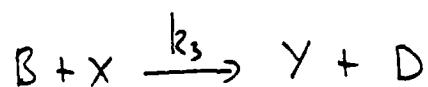
In recent years there has been considerable interest in the behavior of such non-linear chemical systems far from equilibrium⁽⁶⁾. In this section, we wish to illustrate briefly the phenomena that may be encountered when sound is absorbed by a chemical system in a steady state. The example discussed is not comprehensive but displays, in a simple manner, the features that can arise in the sound absorption spectrum.

Acoustic effects in such systems have been studied by Ross and co-workers⁽⁷⁾. The method of analysis followed here is quite similar to the method, discussed by Deutch *et al.*⁽⁸⁾, required to describe the spectrum of light scattered from chemically reacting systems far from equilibrium.

A. The Prigogine-Lefever Mechanism⁽⁹⁾

Consider the model reaction scheme (without back reaction)





where species A, B, and E are considered present in fixed concentrations, and only X and Y are pertinent fluctuating variables.

The rate equations for the concentrations are

$$\frac{dX}{dt} = k_1 A + k_2 X^2 Y - k_3 BX - k_4 X \quad (7.2)$$

$$\frac{dY}{dt} = -k_2 X^2 Y + k_3 BX .$$

A steady state exists for this illustrative reaction scheme when

$$Y_0 = k_3 B / k_2 X_0^2 \quad (7.3)$$

$$X_0 = \frac{k_1 A}{k_4} .$$

In terms of fluctuations in the concentrations from these steady states one has

$$\frac{d\delta X}{dt} = -[k_4 + k_3 B - 2k_2 X_0 Y_0] \delta X + k_2 X_0^2 \delta Y \quad (7.4)$$

$$\frac{d\delta Y}{dt} = +[k_3 B - 2k_2 X_0 Y_0] \delta X - k_2 X_0^2 \delta Y .$$

For simplicity in analysis we assume that all the rate coefficients are equal and that $A=1$. Under these circumstances we have

$$\frac{d\delta\lambda_x}{dt} = -k(1-\beta)\delta\lambda_x + k\delta\lambda_y \quad (7.5)$$

$$\frac{d\delta\lambda_y}{dt} = -k\beta\delta\lambda_x - k\delta\lambda_y$$

where we have introduced the two progress variables

$$\delta\lambda_x = V\delta x \quad \delta\lambda_y = V\delta y \quad (7.6)$$

We know that the relaxation times of this system will be related to the eigenvalues of the matrix \underline{M} , which takes the form

$$\underline{M} = k \begin{bmatrix} (1-\beta) & -1 \\ \beta & 1 \end{bmatrix} \quad (7.7)$$

The two relaxation times which arise are

$$\tilde{\tau}_{\pm}^{-1} = \lambda_{\pm} = \frac{2-\beta}{2} \pm \frac{1}{2} \sqrt{(2-\beta)^2 - 4} \quad (7.8)$$

For $B > 2$, both relaxation times will have a negative real part since $\text{Re}(\lambda_{\pm}) < 0$. For this case the fluctuation will grow exponentially from the steady state signalling that the state is absolutely unstable and hence physically unrealizable.

For $0 < B < 2$, the relaxation time will have positive real parts, indicating that the candidate steady state is stable. However, in this regime, the relaxation times become complex with relaxation times given by

$$\chi_{\pm}^{-1} = \lambda_{\pm} = \frac{2-b}{2} \pm \frac{i}{2} \sqrt{4 - (2-b)^2}, \quad 0 < b < 2. \quad (7.9)$$

The imaginary part of the relaxation time indicates that the concentration variables perturbed from their steady state, for example by passage of a pressure disturbance, will return to equilibrium in an oscillatory manner.

$$\delta\lambda(t) = \delta\lambda(0) \exp[-\lambda' t] \cos[\lambda'' t] \quad (7.10)$$

where λ' and λ'' denote the real and imaginary parts of the eigenvalues of λ respectively.

It is worthwhile remarking that as the point of marginal stability is approached $B \rightarrow (2-)$, the example displays a slowing down in the damping of the chemical mode [$\lambda' \rightarrow 0$] that one might guess would

be manifest in the spectrum $\alpha(\omega)$ as a sharp peak. However, it must be remembered that the treatment presented here has ignored other dissipative transport effects, in particular, diffusion. Sufficiently near the point of instability it is necessary to take these effects into account ⁽⁸⁾, i.e. one cannot rest the analysis on the basis of homogeneous perturbations.

B. Significance of Complex Chemical Relaxation Times

The preceding analysis indicates that for chemical systems in a steady state far from equilibrium, one of the chemical modes will possess a complex eigenvalue in its fluctuation behavior. According to Eq. (7.10) the equation of motion for this mode is given by

(7.11)

$$\frac{d^2 \delta \lambda}{dt^2} = -\omega_c \delta \lambda - \gamma \delta \lambda$$

where ω_c is equal to the imaginary part of the eigenvalue characterizing the mode and γ is equal to the real part of the eigenvalue.

It is apparent from Eq. (7.11) that the chemical mode exhibits wave like behavior. This chemical wave is characterized by frequency ω_c and damping γ . In contrast, when the chemical system is at equilibrium and not in a steady state $\omega_c = 0$.

The consequences of this type of behavior on the frequency dependent compressibility $\kappa_T(\omega)$ can be seen from Eq. (4.13).

In place of the conventional expression

$$\chi_T(\omega) = \chi_T(\infty) + A \frac{\epsilon^{-1}}{\epsilon^{-1} + i\omega} \quad (7.12)$$

one finds

$$\chi_T(\omega) = \chi_T(\infty) + \frac{A}{2} \left[\frac{\gamma + i\omega_c}{\gamma + i(\omega + \omega_c)} + \frac{\gamma - i\omega_c}{\gamma + i(\omega - \omega_c)} \right]. \quad (7.13)$$

One finds that $\kappa_T(\omega)$ contains frequency shifts of $\pm\omega_c$. The chemical wave has effectively added (or subtracted) the frequency of the chemical wave ω_c from the frequency of the imposed pressure wave ω . The pressure relaxation in this case may be regarded as a sort of Raman process with the incident frequency ω , scattered into frequencies $\omega \pm \omega_c$.

The complex part of the compressibility $\kappa_T''(\omega)$ will be

$$\kappa_T''(\omega) = \frac{A\gamma\omega}{2} \left[\frac{1}{(\omega + \omega_c)^2 + \gamma^2} + \frac{1}{(\omega - \omega_c)^2 + \gamma^2} \right]$$

so that the Lorentzian form for the absorption coefficient $[\alpha(\omega)/\omega]$ Eq. (4.17) is replaced by the shifted Lorentzian

$$\frac{d(\omega)/\omega}{2K_T/\omega} = \frac{\pi A}{2K_T/\omega} \left[\frac{\gamma}{(\omega+\omega_c)^2+\gamma^2} + \frac{\gamma}{(\omega-\omega_c)^2+\gamma^2} \right], \quad (7.14)$$

in the limit of low dispersion. It is clear from Eq. (7.14) that the absorption spectrum is shifted by frequency ω_c as a result of the chemical waves.

The simple example considered here clearly indicates that sound absorption is an important potential tool for studying chemical systems in steady states far from equilibrium.

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